

The University of Chicago

**A THERMODYNAMIC STUDY
OF AQUEOUS CADMIUM CHLORIDE
SOLUTIONS**

**A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY**

**DEPARTMENT OF CHEMISTRY
1931**

**By
EDMUND LEROY LIND**

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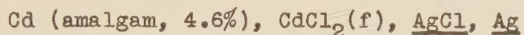


A THERMODYNAMIC STUDY OF AQUEOUS CADMIUM CHLORIDE SOLUTIONS

Introduction

Anomalous behavior of solutions of cadmium chloride makes a knowledge of their activity coefficients highly important. An accurate method for determining these depends upon measurement of the electromotive forces of cells in which aqueous solutions of cadmium chloride serve as electrolyte. Some work has already been done and reported along these lines.

Horsch¹ measured the E.M.F. at 25°C of the cell



in 1919. Lewis and Randall² calculated the activity coefficients for the concentrations used by Horsch. With the exception of the saturated solution and the tenth formal solution, Horsch confined his work to relatively low concentrations. For solutions more dilute than 0.000479 formal, however, Lewis and Randall did not use Horsch's data, but made the assumption that the activity coefficients are the same as those of barium chloride.

In order to secure more information as to the concen-

1. Horsch, J. Am. Chem. Soc., 41, 1787 (1919).

2. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., (1923).

trated solutions, which Horsch scarcely touched, Young and Hartsuch³ measured the E.M.F. of the cell

Cd (amalgam, 10%), CdCl₂(f), AgCl, Ag
at several formalities greater than one-tenth. This work, too, was done at 25°C.

Getman set up cells of the type

Cd (amalgam, 10%) CdCl₂(f), Hg₂Cl₂, Hg
of formalities covering a large part of the range between the saturated solution and 0.00086 formal. He measured the electromotive forces of these cells at 25°C, and reported activity coefficients for cadmium chloride at a number of rounded formalities.⁴ Getman's results do not agree well with those of Horsch, or with those of Young and Hartsuch. The latter two works give concordant results when allowance is made for the difference in amalgam strengths used. Getman did not construct a saturated cell, but included with his own data those for such a cell reported by an earlier worker;⁵ although the value so obtained does not lie on a smooth curve with his own results when plotted.

Since the present research was started, Lucasse⁶ has reported activity coefficients for cadmium chloride obtained from measurements of the electromotive force at 25°C of the

3. Hartsuch, M. S. Dissertation, The University of Chicago (1928).

4. Getman, J. Phys. Chem., 32, 91, (1928).

5. Geheilm, Chem. Zentr., 1, 1853 (1913). Lipscomb & Hulet, J. Am. Chem.

6. Lucasse, J. Am. Chem. Soc., 51, 2597 (1929). Soc. 34, 20 (1916)

cell

Cd (amalgam), CdCl₂(f), AgCl, Ag

The concentration of Lucasse's amalgam is not available,⁷ but the method of preparation of his cells indicates that it was a liquid amalgam. The electromotive forces which he reports also indicate an amalgam concentration in the liquid range.

If the data of Horsch, of Young and Hartsuch, and of Lucasse are all plotted on a graph showing logarithm of concentration against electromotive force, three parallel curves, one for each set of data, are secured. The agreement is good throughout the ranges of concentrations used. Lack of coincidence, of course, arises from differences in amalgam strengths used, and correction for this factor brings about essential agreement in results. Getman's results do not parallel the others when similarly plotted, and this fact made desirable a series of measurements covering the range studied by these workers.

While any liquid or two phase cadmium amalgam will give satisfactory results, the liquid amalgams are inconvenient because a given strength must be very exactly maintained throughout a given research if all cells are to show consistent voltages. This is not true of two phase amalgams, whose advantages are well presented by Hulett:⁸

7. Private communication.

8. Hulett, J. Am. Chem. Soc., 30, 1805 (1908).

"All cadmium amalgams between six and thirteen per cent cadmium have the same potential against an electrolyte because at room temperature any amalgam in this range is made up of two phases, and the composition of the liquid phase depends only on the temperature. When the temperature is fixed, there results one of the most reproducible concentrations we have, and it is immaterial whether such an electrode loses cadmium by oxidation or in other ways."

For these reasons a two phase amalgam was adopted for the present research. A 10 per cent concentration was made in all cases because neither phase of a cadmium amalgam of this strength disappears between 20°C and 30°C, between which temperatures the cells were to be studied.

In general, cells of the type worked with do not maintain their voltage indefinitely, but gradually weaken after a few days. It had been noticed by Young and Hartsuch that a layer of white insoluble matter formed over the amalgam surface of their less concentrated cells, and it seemed possible that the falling off in electromotive force might be connected with the formation of this deposit. One of the objects of the present research was an analysis of this material, and a determination of the conditions responsible for its presence in the cells.

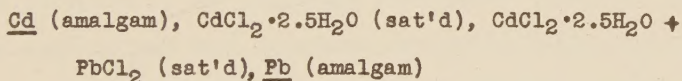
It was thought that oxygen dissolved in the cell electrolyte might be involved. Oxygen has been shown to affect the electromotive forces of some cells, and Gerke⁹ recommends its exclusion as a general practice in the making of electric

9. Gerke, Chem. Rev., 1, 377 (1924-5).

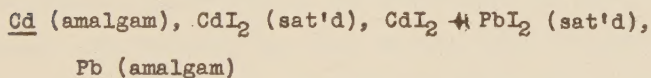
cells. Allmand¹⁰ found that oxygen from the air affected the E.M.F. of cells in which he was studying the electrolytic behavior of cuprous oxide and cupric hydroxide. In the rather special case of the use of sodium ethylate as electrolyte, Danner¹¹ found oxygen very objectionable due to the formation of aldehyde, and consequent poisoning of his hydrogen electrodes.

Vosburgh,¹² in preparing saturated standard cells containing a cadmium-tin amalgam used electrolytes from which the oxygen had been pumped. Cells containing this oxygen-free electrolyte were prepared in two ways. He flushed the gas space above the electrolyte in one group with nitrogen to remove the air, but omitted such precautions with the other group. No effect was noted due to the different gases above the electrolyte in the two sets of cells.

Vosburgh¹³ also studied the effect of air on cells of the type



and



He found no apparent effect due to oxygen from the air in the

10. Allmand, J. Chem. Soc., 95, pt 2, 2151 (1909).

11. Danner, J. Am. Chem. Soc., 44, 2832 (1922).

12. Vosburgh, J. Am. Chem. Soc., 47, 2532 (1925).

13. Vosburgh, *ibid.*, 49, 2222 (1927).

case of the chloride, but thought that a difference of two-tenths of a millivolt between two groups of iodide cells might be due to the presence of air in one of the groups.

Eppley, in an article entitled "An Improvement in the Technique of Setting up Standard Cells,"¹⁴ refers to the use of precautions to remove trapped atmospheric oxygen from between the mercury and the "H" vessel, and air from the inside of this latter, as a useful addition to the procedure of constructing standard cells.

A number of other researches which employed technique for eliminating oxygen from cell electrolytes are described in the literature, but in general these do not afford comparisons of results obtained with and without the use of such precautions. It will be noted that exclusion of oxygen was found valuable in some of the cases cited, and unimportant in others.

14. Eppley, Trans. Am. Elec-Chem. Soc., 53, 149 (1928).

Experimental Procedure

I. Preparation of Materials

Cadmium Chloride. The cadmium chloride used was J. T. Baker's "C.P." grade. Five pounds at a time were dissolved in such a quantity of conductivity water as to yield an approximately saturated solution at the boiling point. The solution was filtered, poured into large Pyrex beakers, cooled, "seeded" with a few very small crystals and allowed to stand. When about a third of the material had crystallized out, the crystals were collected on a filter, dried, and stored in a glass stoppered bottle until needed. Chemical tests for nitrates, sulphates, iron, aluminum, lead, zinc, and copper all gave negative results.¹⁵

Mercury. Mercury of high purity was obtained and was further purified by the following treatment. First it was covered with 10 per cent potassium hydroxide solution and bubbled violently by drawing air through it for several hours. This treatment was to remove any grease and oil which might be present. The mercury was then washed with distilled water, covered with a 25 per cent solution of nitric acid, and the bubbling was repeated. This treatment was to remove metals more active than mercury.

¹⁵. Murray, "Standards and Tests for Reagent and C.P. Chemicals," D. Van Nostrand Co., (1927).

The mercury was again washed and it was dried and distilled according to the method of Hulett and Minchin.¹⁶ For this purpose a special still was designed and blown of Pyrex glass. The still is illustrated in Figure 1. Its design permitted a very small current of air to be drawn through the mercury by a water aspirator pump which was able to maintain a pressure sufficiently low for distillation despite the influx of air. Base metals present in the mercury are oxidized by the air treatment and the noble metals, - gold, silver, and platinum, - do not distil over at the temperature employed.

Finally, the mercury was placed in a large funnel whose stem was drawn to a capillary, and the small droplets emerging were allowed to fall through a column of nitric acid about a meter high. This solution contained about three hundred cubic centimeters of C.P. concentrated nitric acid to a liter of distilled water. The mercury was next thoroughly washed, first with distilled and then with conductivity water, and stored under conductivity water in a stoppered bottle.

Cadmium. J. T. Baker's "C.P." cadmium metal was used. This was distilled under low pressure according to the method of Morse and Jones,¹⁷ as recommended by Wolf and Waters.¹⁸ The metal was placed in a long Pyrex tube which had been sealed at one end. The other end was then drawn down to suitable

16. Hulett and Minchin, *Phys. Rev.*, 21, 389 (1905).

17. *Am. Chem. J.*, 14, 262 (1892); 10, 311 (1888).

18. *Bull. Bur. Standards*, 4, 11, (1907).

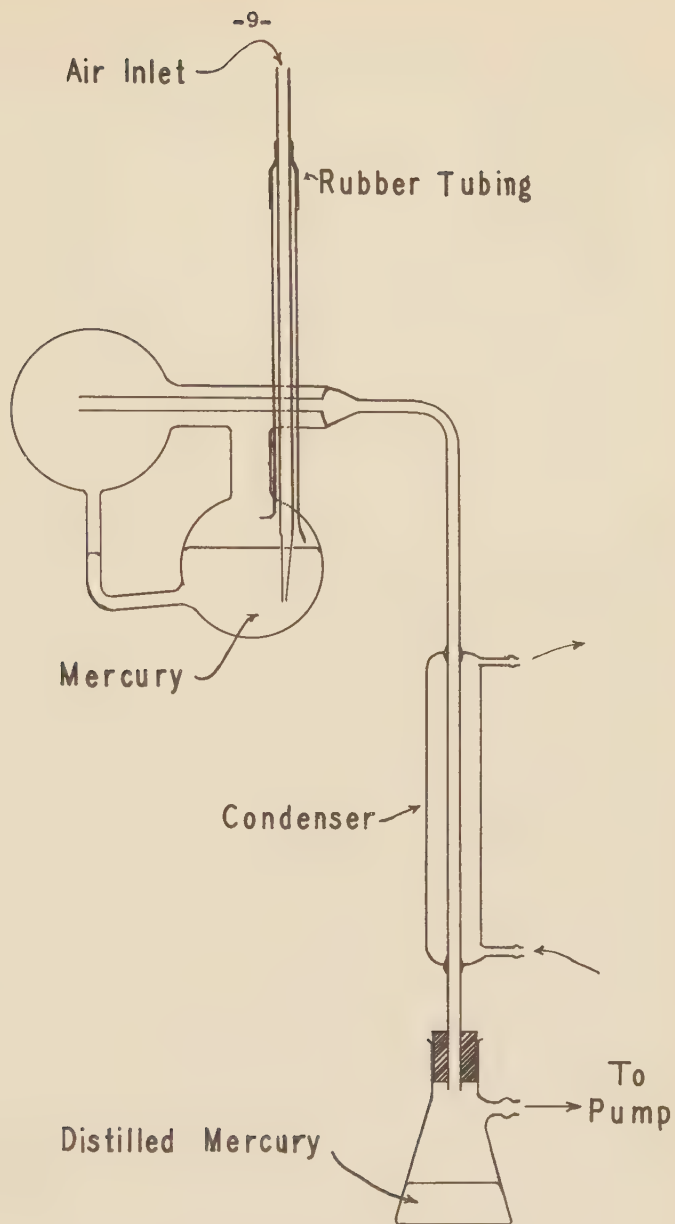


FIG. 1.

size for attachment of pressure rubber tubing, and constrictions were blown to divide the Pyrex tube into three compartments. During the process of distillation, the tube was kept evacuated by means of an oil pump. The closed-end compartment, containing impure metal, was kept at a temperature high enough to melt the cadmium and insure satisfactory vapor pressure for distillation. The middle section was slightly cooler, and the last compartment was not heated.

With the temperature regulation maintained, impurities of higher vapor pressure than cadmium distilled into the cold chamber, purified cadmium condensed in the middle chamber, and impurities of vapor pressure lower than that of cadmium remained in the original compartment. Vacuum was maintained during cooling in order to prevent oxidation of the cadmium. The metal thus obtained was very bright, and showed beautifully defined crystal faces.

Cadmium Amalgam. Cadmium and mercury were weighed out in proper proportions for a 10 per cent amalgam. The mercury was placed in a glass stoppered bottle, the air therein was flushed out with nitrogen, and the cadmium was added. Gentle heat was applied by means of an electric hot plate, and solution was effected without appreciable scum being formed. As explained before, since the amalgam prepared was a two phase amalgam, loss of small quantities of cadmium due to oxidation would not affect its usefulness.

Silver-Silver Chloride Electrodes. These were prepared by essentially the method used by Young and Hartsuch.³ Pure silver oxide was first made by precipitation from silver nitrate solution by means of sodium hydroxide solution. Mallinckrodt's "C.P." materials were used, and the silver oxide thus prepared was thoroughly washed with conductivity water, and kept under conductivity water ready for use.

Small spirals of platinum were sealed into pieces of Pyrex tubing for the electrodes. The exposed ends of the spirals were coated with the silver oxide paste, and the electrodes were heated at 430°C in an electric furnace until the oxide had been entirely reduced to metallic silver. The process was repeated two or three times, until the platinum was well-covered, and, indeed, its spiral form entirely concealed by the white, porous silver. Young and Hartsuch had first deposited a thin coat of electrolytic silver before forming the porous silver by reduction of the oxide, but this practice was found to give electrodes slightly less reproducible.

The electrodes were cooled slowly to avoid formation of strains in the silver. Since Pyrex does not make a tight seal with platinum, small bits of paraffin were then dropped into the tubes into which the spirals had been sealed. Space between platinum and Pyrex was sealed off by carefully melting this paraffin; care was taken not to completely cover the platinum and thus make electrical contact impossible. Platinum electrodes for making contact with amalgam in the cells

were similarly treated with paraffin.

A coating of silver chloride was formed on the white, porous silver by making four of the electrodes anode in a solution of about the strength to be used in the cells. This was to prevent inclusion in the electrodes of electrolyte of unknown concentration. Enough solution was used to avoid appreciable change in concentration of cadmium chloride due to electrolysis. Ten milliamperes of current were used, and deposition was continued for five hours. Local changes in concentration around the electrodes were avoided by circulating the solution by means of an electric stirrer. The electrodes were kept in the solution after preparation until construction of the cells. This was always within a few hours after completion of the electrolysis.

II. Study of Effect of Oxygen

The white deposit previously mentioned was studied before most of the cells were made whose voltages are given in this paper. The material was found to appear whenever cadmium chloride solutions of not too great concentration came in contact with cadmium amalgam. Action of an electric cell is therefore not required for its formation. Test tubes of soft glass, Pyrex, quartz, and paraffin-coated glass were filled with amalgam and cadmium chloride solution. Deposit formed in all cases in apparently equal quantities, and there is thus no reason to suppose that the material of the containing vessel enters into the reaction. Tests were conducted with solutions approximately 0.00001, 0.0001, 0.001, 0.01, 0.1, 0.5, 1, 2, 3, 4, 5, and 6 formal respectively. All formalities from 3 down yielded the white precipitate, those between 3 and 0.5 most voluminously. Even after ten months no deposition occurred in the stronger solutions. Deposition did not begin in the tubes containing 1 and 2 formal solution until several days after it was apparent in the more dilute solutions and in the case of the 3 formal solution not until still later, although a heavy deposit developed in time.

Qualitative tests made on the material showed cadmium and chlorine but no trace of mercury. Solutions allowed to stand over mercury instead of over amalgam showed no deposit, thus eliminating the mercury as a necessary catalyst to the reaction. Furthermore, deposit did form when solutions stood

over pure metallic cadmium.

While these tests were going on, analysis of the white material was undertaken. Only very small quantities of the material were available, but it was possible to get good enough agreement between duplicate analyses for purposes of identification. Chlorine was determined gravimetrically by precipitation with silver nitrate. Cadmium was determined according to Treadwell-Hall's recommendation.¹⁹ Two samples were treated with a slight excess of sulphuric acid, and the solutions were evaporated to dryness and until no further fumes of sulphur trioxide came off. The sulphates were heated to constant weight.

The results obtained indicated a formula CdOHCl for the material. To determine the amount of OH (and confirm its presence at the same time), samples of the substance were taken up in known quantities of standard hydrochloric acid, the solutions so formed were back-titrated with standard base, and the lost acidity was calculated as OH in accordance with the equation



The analysis for OH was consistent with the formula CdOHCl already suggested.

19. Treadwell-Hall, "Quantitative Analysis," p. 190, John Wiley and Sons (1930).

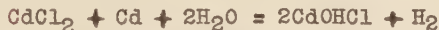
Analysis: Substance, 0.1540, 0.0748; Cl, 0.0324,
0.0159. Calculated for CdOHCl, 21.51. Found, 21.05, 21.20.

Analysis; Substance, 0.1266, 0.0902; Cd, 0.0865,
0.0618. Calculated for CdOHCl, 68.18. Found, 68.32, 68.50.

Analysis: Substance, 0.1080, 0.0994; OH, 0.0111,
0.0110. Calculated for CdOHCl, 10.31. Found, 10.27, 11.10.

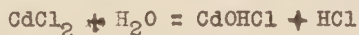
Interest next centered upon the question of the substances necessary for the formation of the basic chloride.

One possible reaction is



If this reaction occurs, enough hydrogen should be set free, judging from the quantities of deposit formed, to saturate the solution, and develop a measurable pressure in a small containing vessel. Accordingly, a manometer was blown onto a flask, into which were then sealed some amalgam and cadmium chloride solution. The flask was kept at constant temperature for a number of days, and deposit formed as usual, but no observable pressure developed. It thus appears that the above reaction was not occurring.

A second possibility would be the following:



This reaction was considered not probable inasmuch as metallic cadmium, shown to be necessary for formation of the deposit, does not enter in. Of course, the metal might simply catalyze the reaction. The equation predicts a definite increase in hydrogen ion concentration. No such increase could be detected, and the reaction is therefore eliminated from consideration.

Finally, there is the possibility that oxygen dissolved by the solution from the air might be responsible for the formation of the basic chloride. The following equation would then apply:



To test for this reaction, the apparatus illustrated in Figure 2 was used. Some cadmium chloride solution was placed in the flask, and a test tube containing amalgam was so lowered into the flask that no solution could reach the amalgam. The top of the flask was then sealed off as shown and the side-arm was sealed to a vacuum line and the flask's contents were very thoroughly evacuated. The flask was agitated during pumping, and its contents were kept warm enough to maintain the amalgam in a liquid state and thus insure its thorough evacuation of air. The flask was sealed off under vacuum, inverted so as to mix amalgam and solution, and well shaken.

Shaking was repeated for several days, but no deposit formed, the liquid remaining very clear and the amalgam bright. After a week the flask was opened and oxygen was bubbled through the solution. Precipitation started within a few hours. Oxygen was thus proved to be necessary for the formation of the deposit.

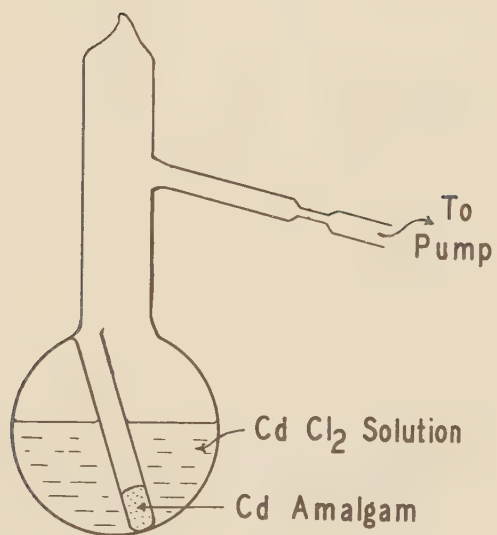


FIG. 2.

III. Preparation of Cells

Cadmium chloride solutions for each set of cells were made up to approximately the strength desired by dilution of a standard concentrated stock solution which had been prepared from the crystallized salt. Before being run into the cells the solution was evacuated, then allowed to absorb nitrogen, evacuated again, and again treated with nitrogen. Agitation was resorted to both in the pumping and during saturation with nitrogen in order to facilitate the processes.

The nitrogen used was a water-pumped product furnished by the Air Reduction Sales Company and was stated to be at least 99.7 per cent pure. Before admission to the solution or cells, it was passed over copper turnings kept hot by means of an electric furnace in order to remove traces of oxygen. After use the turnings were reduced by means of a stream of hydrogen.

The cells used were of "H" type. Figure 3 is a full-size illustration of these cells after preparation, and it shows the details of electrode construction already described.

Amalgam was first placed in the cells, which were then evacuated of air and filled with nitrogen. The platinum electrode for establishing contact with the amalgam was then inserted, electrolyte was forced in under nitrogen pressure, and the silver-silver chloride electrode was placed in the other leg of the cell. The stoppers used were of paraffin-dipped cork, and the space above them was filled with paraffin as il-

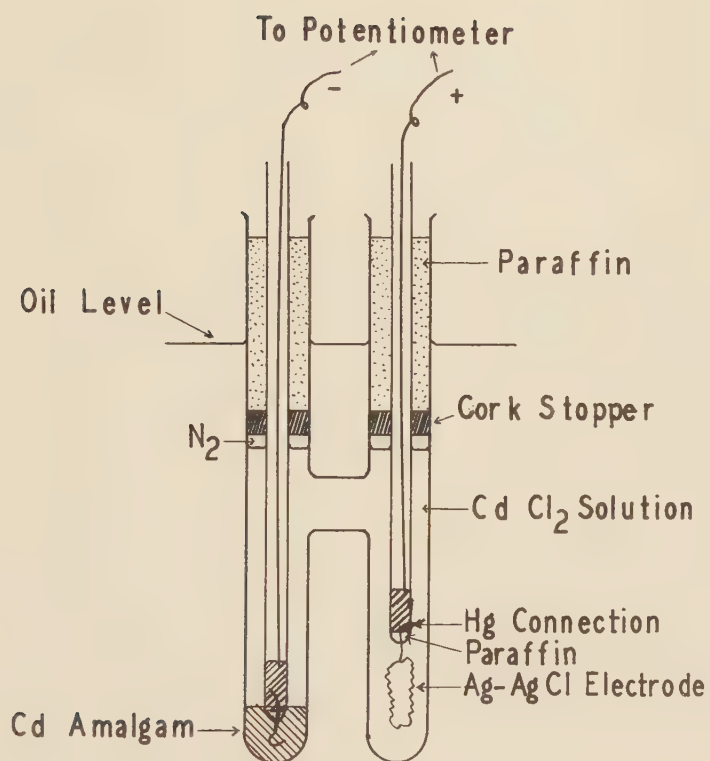


FIG. 3.

lustrated. The cells were immersed deeply enough in the thermostat to prevent distillation to projecting parts on occasions when room temperature was lower than the thermostat temperature.

At the time the cells were filled, portions of electrolyte were run into weighed bottles for analysis of cadmium chloride content.

The thermostat used was filled with oil, because the conductivity of thin films of water on the glass cells is appreciable and would have hastened the deterioration of their contents. "Wemco" transformer oil was secured from the Westinghouse Electric and Manufacturing Company for this purpose. The regulator was mercury type, specially designed, and maintained constant temperature within plus or minus one hundredth of a degree.

No previous work had been done on the temperature coefficient of the type of cell being studied, and, accordingly, most of those constructed were measured at 20°C, 25°C, and 30°C. The temperatures were read on a thermometer graduated in tenths of a degree which had been compared with a thermometer calibrated and certified by the Bureau of Standards. Temperature variations were read on a Beckmann thermometer.

All E.M.F. measurements were made with a Leeds and Northrup type K potentiometer which had previously been calibrated. The working battery was a lead storage cell, and an Eppley cell, No. 34482 was used as standard.

Two type R Leeds and Northrup galvanometers were used, one for cells of low concentration and one for those of higher concentration. This was found desirable because of different cell resistances in the dilute and concentrated ranges.

Potentiometer, working and standard cells, galvanometers, and the "aerial" supporting the connecting wires were shielded from stray currents by an equipotential shield after the method of White.²⁰ All leads were supported on paraffined glass rods.

Four cells, or in a few cases, three, were made up from solutions of each concentration used. The vacuum technique described entirely prevented the formation of basic cadmium chloride in some sets, and in no case was more than a very small quantity formed, even after the cells had stood for months. Cells thus prepared in the absence of oxygen agreed well with those made by Young and Hartsuch with no precautions against atmospheric oxygen.

It was definitely observable, however, that cells containing no oxygen agreed better among themselves, and showed much slower voltage drop on aging than cells prepared in the presence of air.

Cells of one-tenth formal concentration or greater in a given set varied among themselves by less than a tenth of a millivolt, and in most cases by less than five-hundredths of

20. White, J. Am. Chem. Soc., 36, 2011 (1914).

a millivolt. The members of one set showed a maximum variation among themselves of one-hundredth of a millivolt during eight days of observation, although their voltage fell during that time a total of five-hundredths of a millivolt.

Cells containing more dilute solutions did not agree so well. Variations were less than a millivolt, however, except in the cases of the 0.000117 and 0.000333 formalities. In this region, the effect of any side reactions occurring in the cell is very rapid, with resultant poorer agreement among the cells of a set, and lower precision in measurement.

Two cells of one group contained small Pyrex capsules into which had been sealed half-inch lengths of iron wire. When the cells of this group showed lowered voltage after standing for a few days, the solution above the amalgam in these cells was stirred by agitating the iron-filled capsules by means of a magnet. Upon measurement, the cells were then found to have recovered a large part of the lost voltage. It thus appears that where it is desired to observe cells over a period of time, some such technique as that employed will be valuable as a means of eliminating polarization around the electrodes.

It was found more difficult to prepare good silver-silver chloride electrodes in dilute than in more concentrated solutions. Inasmuch as cells agreed less well with each other in dilute regions, also, it appeared that part of the difficulty might be due to discrepancies among the electrodes.

To investigate this matter, the silver-silver chloride electrodes of two cells showing half a millivolt difference in E.M.F. were interchanged. The cells when measured were then found to have interchanged voltages and it is thus established that differences among the silver-silver chloride electrodes are an important factor in lack of agreement among the different cells of a set. The results of this test also verify the statement previously made that the two phase amalgam used possesses a very definite potential at fixed temperature.

In two respects the measurements obtained in this research are more consistent among themselves than were those of Horsch and of Lucasse. First, the individual cells of a set varied less among themselves, and, second, deterioration was less rapid. The desirability of excluding oxygen from the cell electrolytes and amalgam therefore seems well established.

Experimental Results

I. Tabulation of Results

In Table I are listed the cell concentrations used, the electromotive forces at the three temperatures at which work was done, and calculated values of γ , the activity coefficient, and of $\Delta E/\Delta T$, the temperature coefficient of the cells. The concentration, or formality, f , is expressed in formula weights of cadmium chloride, CdCl_2 , per 1000 grams of water.

TABLE I

f	$E(20^\circ\text{C})$	$E(25^\circ\text{C})$	$E(30^\circ\text{C})$	γ	$\Delta E/\Delta T$
0.000117	0.89766	0.90116	0.90672	1.08	+0.000906
0.000333	.86325	.86646	.86931	.9 ₃₇	.000606
.000786	.83749	.84003	.84353	.78 ₈	.000604
.00573	.77252	.77453	.77632	.59 ₂	.000380
.0503	.71716	.71813	.71907	.291 ₆	.000191
.1010	- - -	.70255	- - -	.217 ₆	- - -
.2164	- - -	.68712	- - -	.151 ₆	- - -
.3500	- - -	.67815	- - -	.118 ₃	- - -
1.030	.66100	.66124	.66107	.062 ₃	+0.000007
1.507	.65480	.65478	.65475	.0503 ₈	-0.000005
3.258	.64240	.64220	.64192	.032 ₃	.000048
6.397	.62625	.62591	.62559	.025 ₁	.000066

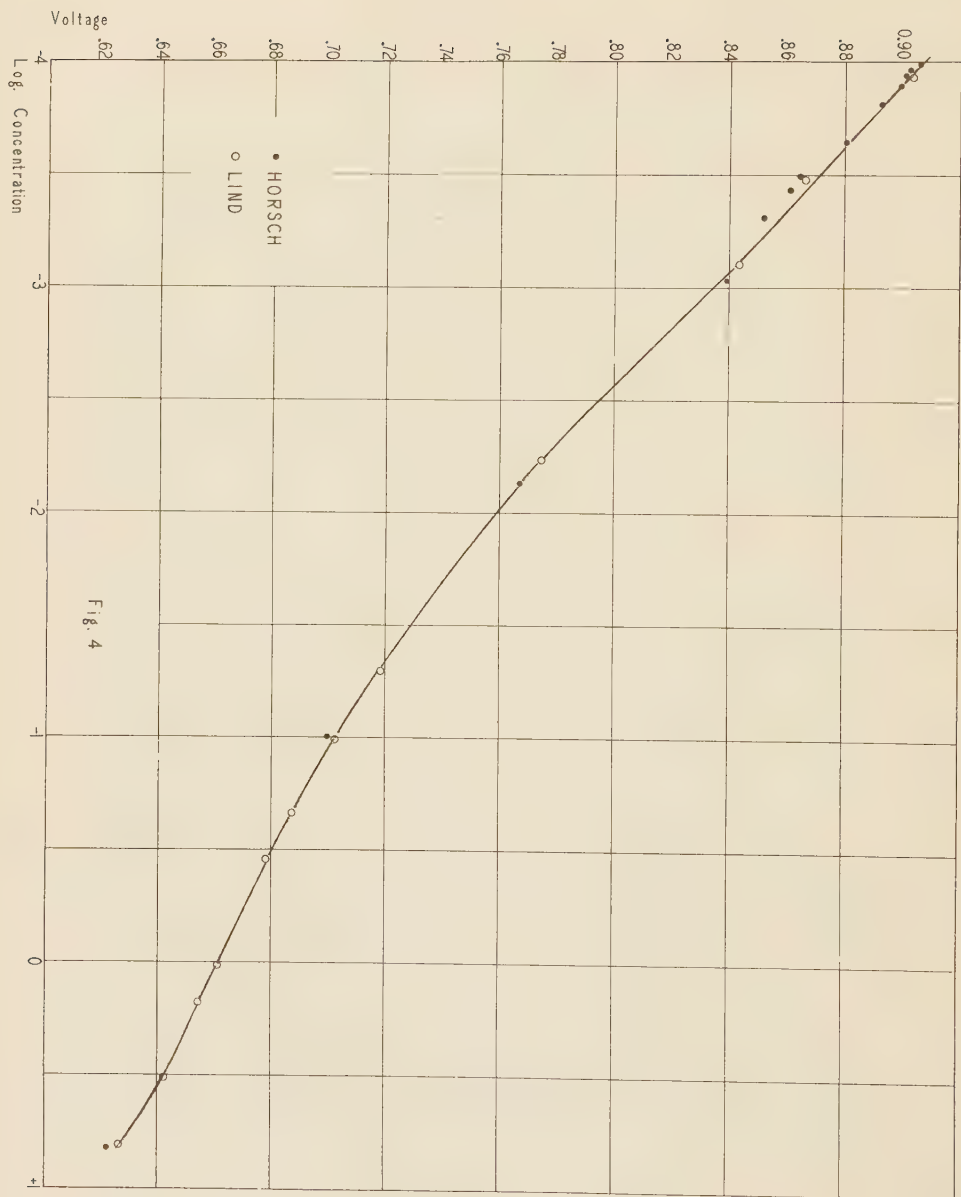
II. Calculation of Activity Coefficients

Figure 4 is a plot of the measured electromotive forces at 25°C plotted against the logarithm of the formality. On this same graph are given the results of Horsch. With the exception of the saturated and tenth formal solutions, Horsch's formalities were all very low, although the logarithmic plotting spreads them out over an apparently very large part of the total possible range. Actually, of course, the more concentrated solutions, which he scarcely touched, comprise the major part of the field, and these constituted the main interest of the present work.

The graph brings out the essential parallelism between Horsch's results and the writer's. The cells of low electrolyte concentration made in the present research were set up partly to make sure that this parallelism, already evident in the concentrated regions, carried out to greater dilution.

Since Lewis and Randall had already calculated activities based on Horsch's data, it was decided to use their 0.0995 formal solution as basis for calculating the activities for the present research.* This would simply involve using

*It is recognized that the absolute values of the activity coefficients given by Lewis and Randall are not necessarily correct. For thermodynamic calculations, however, only the relative values at the various concentrations are needed. Consequently the basis adopted is highly satisfactory, and activities so calculated meet all requirements.



the same activity coefficient for a 0.0995 solution as they did, and calculating coefficients for other formalities on the basis of this value and the electromotive forces of the cells.

The first step necessary was the plotting of logarithmic concentration against $0.088716 \log f$ for all Lewis and Randall's values. The curve thus established differs from the curve of Figure 4 only by a vertical displacement. That this is true is evident from the following considerations:

$$E = E^{\circ} - \frac{RT}{2F} 2.3026 \log 4(vf)^3 \quad (1)$$

where E is the observed E.M.F., E° that for a cell using hypothetical formal solution, R is the gas constant, T the temperature, and F the faraday. Substituting appropriate values for R , T , and F , and rearranging, gives

$$E = E^{\circ} - 0.088716 \log 4^{1/3}vf \quad (2)$$

$$= -.088716 \log vf \text{ plus a constant} \quad (3)$$

The terms are all voltages, and the results of the present research can be brought to the desired basis by determining the magnitude of the vertical displacement necessary to bring the curve so plotted and the curve of the writer's data, Figure 4, to coincidence at 0.0995 formal, and then subtracting the amount so determined from all voltages found at 25°C in the present research.

Thus, interpolation in the writer's data shows that at 0.0995 formal, a cell would have an E.M.F. equal 0.70287. In this range of concentration, interpolation of high precision is possible where mathematical methods are used. Inasmuch as the corresponding value on the reference graph is 0.14742, the difference between these two values, or 0.55545 volts, is to be subtracted from the E.M.F.'s of the present research. This difference is due to constants dropped in equation (3), and to difference in amalgam strengths used in the two researches, and has no bearing on the activities.

The subtraction leaves the cell voltages on the same basis relative to each other, and places the interpolated voltage of the 0.0995 formal concentration, but not the others, on exactly the same basis as Horsch's corresponding cell. Activity coefficients are then readily calculated from the relation that

$$E' = -0.088716 \log \sqrt{f} \quad (4)$$

where E' is the adjusted voltage, as just explained, or, mathematically,

$$E' = E - 0.55545 \quad (5)$$

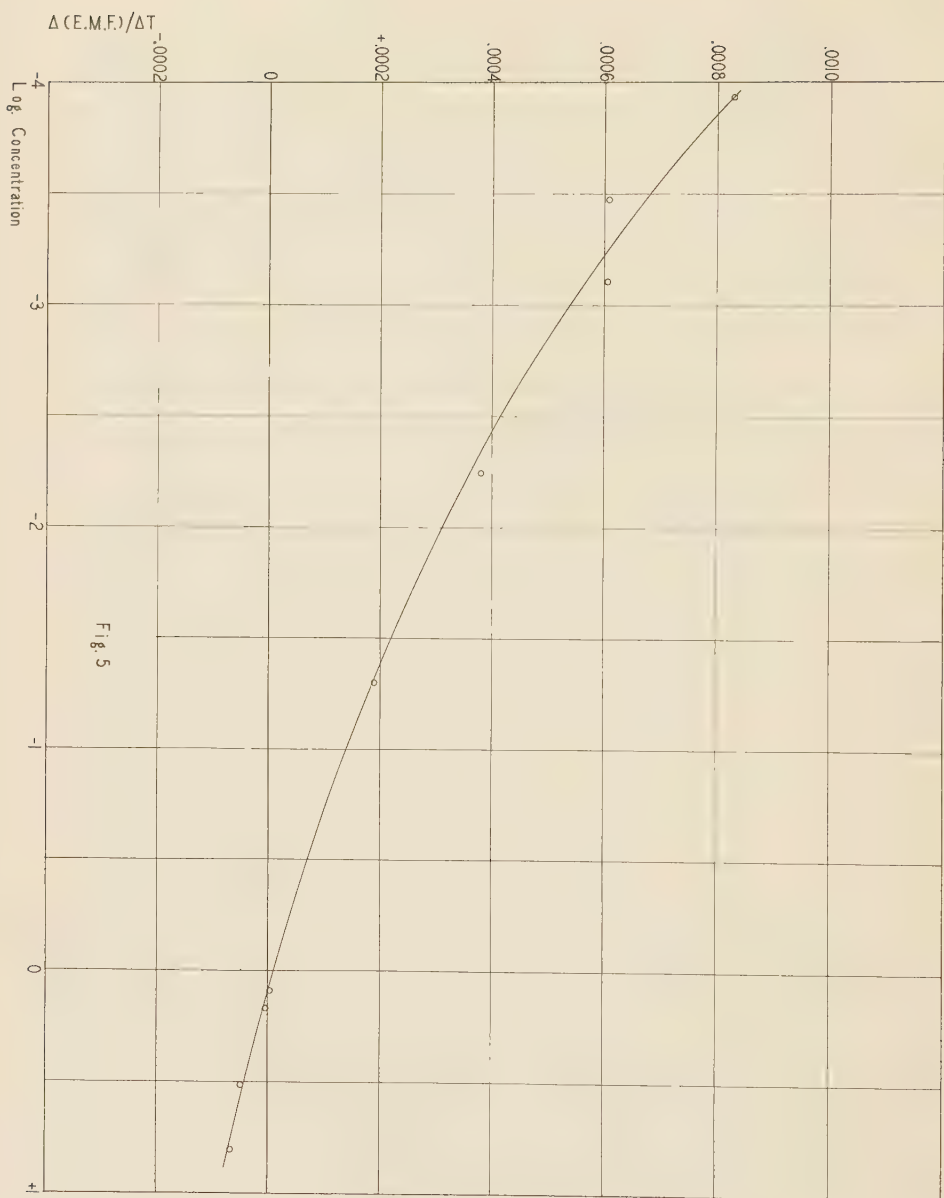
The activity coefficients presented in Table I were calculated in the manner just described. It has already been mentioned that the results of Getman were at variance with those of Lewis and Randall. The present work does not check Getman's values. On the other hand, it does agree well with the limited data of Lewis and Randall except in the most di-

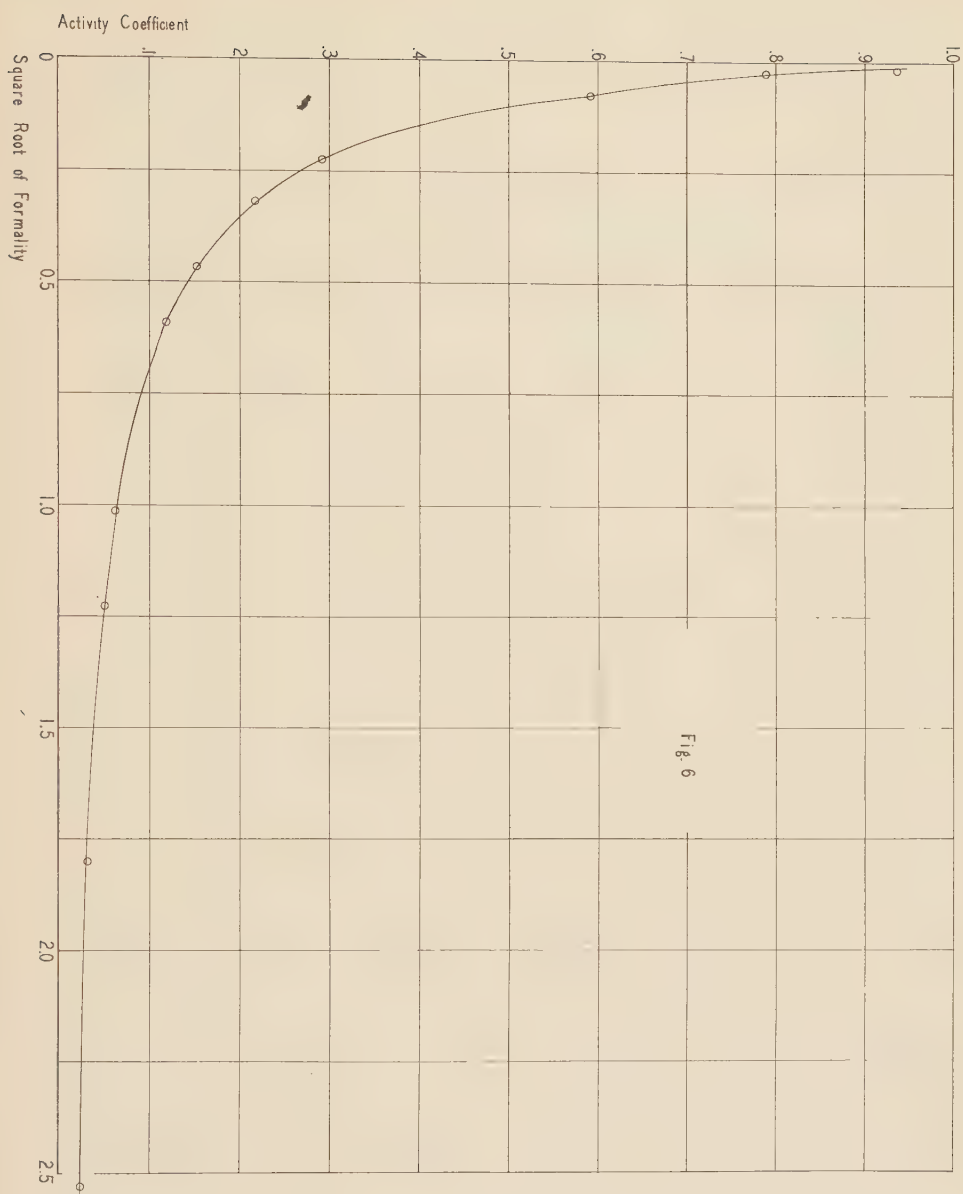
lute regions, where they made the assumption that the activities of cadmium chloride solutions were the same as those of barium chloride. The assumption was made because of a feeling that the solubility of silver chloride in these regions made electromotive force measurements valueless. The reported activities of Lucasse are also in agreement with those determined in this research.

The very good agreement between the results of the present research, and the values given by Lewis and Randall and by Lucasse indicates that the problem of the activity coefficients of cadmium chloride has now been satisfactorily solved. The values reported by Getman appear to be definitely eliminated from further consideration.

It is interesting to compare the very low activity coefficients of cadmium chloride with the values for such electrolytes as sodium chloride and sulphuric acid. Values for cadmium chloride read from the curve, Figure 6, are listed in Table II, together with values given by Lewis and Randall for sodium chloride and sulphuric acid.

Activity coefficient was formerly called the thermodynamic degree of dissociation. In light of modern theories, we are reasonably sure that low activity coefficients are not due entirely to small degrees of dissociation. It is not certain that degree of dissociation plays any role at all in the cases of such electrolytes as sodium and cadmium chlorides. Nevertheless, the very low values found are interesting and





significant, whatever may be the ultimate explanation of the facts.

TABLE II

f	r , NaCl	r , CdCl ₂	r , H ₂ SO ₄
0.01	0.922	0.510	0.617
0.1	.798	.220	.313
1.0	.650	.064	.150
2.0	.661	.041	.147
3.0	.704	.031	.166
4.0	.765	.027	.203
5.0	.852	.025	.242

III. Temperature Coefficients

Since no data was available concerning the temperature coefficients of cells of the type worked with in this research, it seemed worth while to make measurements at several temperatures. The experimental data, and the temperature coefficients, $\Delta E/\Delta T$, calculated from the data, are listed in Table I. The results are shown graphically in Figure 5. It is interesting to note that the temperature coefficients for these cells are very small indeed, actually changing sign at about 1.29 formal.

It is not possible to calculate the ΔH for the reaction of cells which contain two phase amalgams, because of changes in the phase concentrations with temperature. If sufficiently precise data could be obtained at several formalities, it would be possible, however, to obtain differential heats of dilution. In this case, the data revealed that the heats of dilution are small -- indeed, so small that they can not be evaluated from data even of the precision possible with cells of this type.

Summary

1. A technique has been described for setting up cells of the type

Cd (amalgam, 10%), CdCl₂ (f), AgCl, Ag
in the absence of atmospheric oxygen. By means of this technique, cells have been constructed using concentrations of cadmium chloride solution covering the range between one ten-thousandth formal and the saturated solution, and the electromotive forces have been measured at 20°C, 25°C, and 30°C.

2. From the experimental data, activity coefficients have been calculated for cadmium chloride solutions over the range of concentrations investigated.

3. The temperature coefficients of the cells have been evaluated between 20°C and 30°C. These coefficients have been found to be very small, changing sign at a definite concentration of electrolyte.

4. The presence of atmospheric oxygen has been shown to lead to the formation of an insoluble basic chloride of cadmium in the cells, and to hasten their deterioration. The composition of this material has been shown by analysis to correspond to the formula CdOHCl. It appears that the presence of oxygen in the more dilute electrolytes may invalidate results by producing effects of appreciable magnitude before

the cells reach temperature equilibrium with the thermostat, and therefore before the E.M.F. measurements are taken.

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